.

PCT

(21) International Application Number:

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

- (51) International Patent Classification ⁶: WO 96/35819
 C22F 1/04
 A1
 - (43) International Publication Date: 14 November 1996 (14.11.96)

PCT/US96/05327

- (22) International Filing Date: 24 April 1996 (24.04.96)
- (30) Priority Data: 438,784 11 May 1995 (11.05.95) US
- (71) Applicant (for all designated States except US): KAISER ALU-MINUM AND CHEMICAL CORPORATION [US/US]; 6177 Sunol Boulevard, Pleasanton, CA 94566 (US).
- (72) Inventor: and
- (75) Inventor/Applicant (for US only): DORWARD, Ralph, C. [US/US]; 5228 Kathy, Livermore, CA 94550 (US).
- (74) Agents: COOPER, George, M. et al.; Jones, Tullar & Cooper, P.C., P.O. Box 2266, Eads Station, Arlington, VA 22202 (US).
- (81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

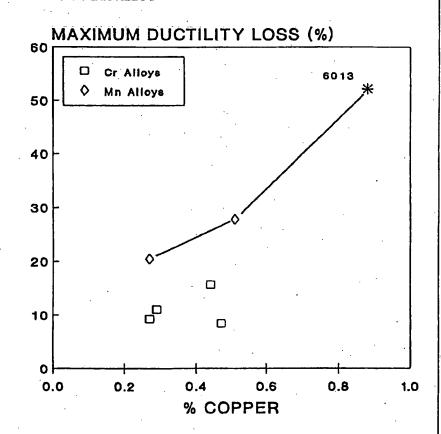
Published

With international search report.

(54) Title: IMPROVED DAMAGE TOLERANT ALUMINUM 6XXX ALLOY

(57) Abstract

A method of producing an aluminum product having high formability, high fracture toughness, high strength and improved corrosion resistance, the method comprising: (a) providing stock including an aluminum base alloy consisting essentially of about 0.7 to 1.0 wt.% silicon, not more than about 0.3 wt.% iron, not more than about 0.5 wt.% copper, about 0.8 to 1.1 wt.% magnesium, about 0.3 to 0.4 wt.% manganese, and about 0.5 to 0.8 wt.% zinc. the remainder substantially aluminum, incidental elements and impurities; (b) homogenizing the stock; (c) hot rolling; (d) solution heat treating; (e) cooling by quenching; and (f) artificially aging to produce a T6 temper in the aluminum product. The figure shows ductility loss as a function of the amount of copper in alloys containing either manganese or chromium and zinc relative to alloy 6013.



BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

	•		_		
AM	Armenia	GB	United Kingdom	· MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	1E	Ireland .	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RÜ	Russian Federation
CA	Canada .	KP	Democratic People's Republic	SD	Sudan
CF	Central African Republic		of Korea	SE	Sweden
CG	Congo	KR	Republic of Korea	SG	Singapore
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LR	Liberia	SZ	Swaziland
CS	Czechoslovakia	LT.	Lithuania	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	LV	Latvia	TJ	Tajikistan
DK	Denmark	MC	Monaco	TT	Trinidad and Tobago
ER	Estonia	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML	Mali -	US	United States of America
FR	France	MN	Mongolia	UZ	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

WO 96/35819

25

30

IMPROVED DAMAGE TOLERANT ALUMINUM 6XXX ALLOY

BACKGROUND OF THE INVENTION

1. Field of Invention

This invention relates to aluminum alloys suitable for use in aircraft, automobiles, and other applications and to improved methods of producing such alloys. More specifically, it relates to a method of making an improved aluminum product, particularly useful in aircraft applications, having improved damage tolerant characteristics, including improved corrosion resistance, formability, fracture toughness and strength properties.

15 2. <u>Description of the Related Art</u>

Workers in the field have used heat treatable aluminum alloys in a number of applications involving relatively high strengths such aircraft fuselages, vehicular members and other applications. Aluminum alloys 6061 and 6063 are among the most popular heat treatable aluminum alloys in the United States. These alloys have useful strength and toughness properties in both T4 and T6 tempers. They lack, however, sufficient strength for most structural aerospace applications.

More recently, Alloys 6009 and 6010 have been used as vehicular panels in cars and boats. These alloys and their products are described in U.S. Pat. No. 4,082,578, issued April 4, 1978 to Evancho et al. In general, alloy 6010 includes 0.8 to 1.2 wt.% Si, 0.6 to 1.0% Mg, 0.15 to 0.6 wt.% Cu, 0.2 to 0.8 wt.% Mn, balance essentially aluminum. Alloy 6009 is similar to alloy 6010

10

15

20. ...

25

30

except for lower Si at 0.6 to 1.0 wt.% and lower Mg at 0.4 to 0.6 wt.%.

In spite of the usefulness of the 6009 and 6010 alloys, these alloys are generally unsuitable for the design of commercial aircraft which require different sets of properties for different types of structures. Depending on the design criteria for a particular airplane component, improvements in fracture toughness and fatigue resistance result in weight savings, which translate to fuel economy over the lifetime of the aircraft, and/or a greater level of safety.

To meet this need, workers in the field have attempted to develop alloys having improved impact and dent resistance as well as substantial toughness. For example in U.S. Pat. No. 4,589,932, issued May 20, 1986 to Park describes a 6013 alloy which includes 0.4 to 1.2 wt.% Si, 0.5 to 1.3 wt.% Mg, 0.6 to 1.1 wt.% Cu, 0.1 to 1% Mn, the balance essentially aluminum. Similarly, Japanese Patent Application Kokai No. 60-82643 describes an alloy which includes 0.4 to 1.5 wt.% Si, 0.5 to 1.5 wt.% Mg, 0.4 to 1.8 wt.% Cu, .05 to 1.0 wt.% Mn, 1.0 to 6.0 wt.% Zn which emphasizes adding copper to reduce intercrystalline cracks. new generation of alloys 6XXX characterized by relatively high copper levels provide strength advantage. a Unfortunately, the high copper contents also increased produce susceptibility intergranular corrosion. Corrosion of this type causes strength degradation in service, but more importantly, greatly detracts from fatigue resistance.

. 2

10

15

20

25

30

35

Corrosion damage has been a perennial problem in today's aircraft, and the fuselage is the prime location for corrosion to occur. Improvements in corrosion resistance, therefore, are often sought with or without weight savings. Thus, the new generation of 6XXX alloys are generally unsuitable aircraft applications because susceptibility to intergranular corrosion caused by high copper levels as discussed in Chaudhuri et al., Comparison of Corrosion-Fatigue Properties of 6013 Bare, Alclad 2024, and 2024 Bare Aluminum Alloy Sheet Materials, JMEPEG (1992) 1:91-96.

Another approach taken in U.S. Pat. No. 4,231,817, issued Nov. 4, 1980 to Takeuchi et al. and Japanese Patent Application Kokai Nos. 55-8426 and 53-65209 which generally describe 6061 and 6063 type alloys which have added zinc. Although the added zinc is reported to improve corrosion resistance, these alloys lack sufficient strength for most structural aerospace applications:

Turning now to formability, many aerospace alloys such as 2024 and 7075 are formed in the annealed O temper or freshly quenched W temper. Forming in the O temper requires, however, a subsequent solution heat treatment operation, which usually introduces distortion problems. Forming in the W temper alleviates the distortion concern, but sheet in this condition hardens as it naturally ages, so either the delay time between solution heat treating and forming must minimized, or the material must be stored in a freezer until it is ready to be formed. In contrast, a sheet material that formability in the stable T4 condition circumvents all of these potential problems because the

15

20...

25 -

30

35

manufacturer need only age to the T6 temper after making the part. It is therefore desirable for the aerospace alloy to have good formability in the stable T4 condition.

In sum, a need remains for an alloy having improved resistance to corrosion and yet maintains the desirable strength, toughness, and T4 formability properties exhibited by the 6013 type alloys. Accordingly, it is an object of this invention to provide such an alloy.

SUMMARY OF THE INVENTION

The present invention provides a method of producing an aluminum product comprising: providing stock including an aluminum base alloy consisting essentially of about 0.6 to 1.4 wt.% silicon, not more than about 0.5 wt.% iron, not more than about 0.6 wt.% copper, about 0.6 to 1.4 wt.% magnesium, about 0.4 to 1.4 wt.% zinc, at one least element selected from the consisting of about 0.2 to 0.8 wt. % manganese and about .05 to 0.3 wt.% chromium, the remainder substantially aluminum, incidental elements and impurities; homogenizing the stock; hot working, solution heat treating; and quenching. product can then either be naturally aged to produce an improved alloy having good formability in the T4 temper or artificially aged to produce improved alloy having high strength and fracture toughness, along with improved corrosion resistance properties.

The foregoing and other objects, features, and advantages of the invention will become more readily apparent from the following detailed description of preferred embodiment which proceeds with reference to the drawings.

15

20

25

30

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing ductility loss as a function of the amount of copper in alloys containing either manganese or chromium and zinc relative to alloy 6013.

FIG. 2 is a graph showing the effect of copper and zinc on the strength of alloys containing either manganese or chromium.

DETAILED DESCRIPTION OF THE INVENTION

The high formability, high fracture toughness, high strength, and enhanced corrosion resistance properties of the alloy of the present invention are dependent upon chemical composition that is closely controlled within specific limits as set forth below and upon a carefully controlled heat treatment. composition limits, fabrication, and heattreatment procedures required to produce the invention alloy stray from the limits set forth below. the desired combination of formability, fracture toughness, strength and corrosion resistance properties will not be achieved.

The aluminum alloy of the present invention consists essentially of about 0.6 to 1.4 wt.% silicon, not more than about 0.5 wt.% iron, not more than about 0.6 wt.% copper, about 0.6 to 1.4 wt.% magnesium, about 0.4 to 1.4 wt.% zinc, at least one element selected from the group consisting of about 0.2 to 0.8 wt.% manganese and about 0.5 to 0.3 wt.% chromium, the remainder substantially aluminum, incidental elements, and impurities.

WO 96/35819 PCT/US96/05327

6

The preferred range of silicon is about 0.7 to 1.0 wt.%. At least about 0.6 wt.% is needed to provide sufficient strength while amounts in excess of 1.2 wt.% tend to produce an alloy that is brittle in the T6 temper. Iron can be present up to about 0.5 wt.% and preferably below about 0.3 wt.%. Higher levels of iron tend to produce an alloy having lower toughness. The preferred range of magnesium is about 0.8 to 1.1 wt.%. At least about 0.6 wt.% magnesium is needed to provide sufficient strength while amounts in excess of about 1.2 wt.% make it difficult to dissolve enough solute to obtain sufficient age hardening precipitate to provide high T6 strength.

5

10

15

20

25 .

30

35

I have found that I can produce an improved alloy sheet, suitable for aircraft fuselage skin which is particularly resistant to corrosion but still maintains high strength, high fracture toughness, and good formability. I do this by taking a 6013 type alloy and greatly reducing its copper content while also adding significant amounts of zinc. In my improved product, if copper exceeds 0.6 wt.%, the products become more prone to corrosion problems. I prefer to keep copper levels below about 0.5 wt.%. For example, as shown in FIG. 1, by increasing copper from 0.5 0.9 wt.%, general corrosion damage (measured by ductility loss) will increase by as much as 50%. Some copper below these limits, however, is desirable to improve strength while greatly adversely affecting corrosion resistance.

Reducing the amount of copper in the new alloy has the disadvantage of reducing strength as shown in FIG. 2. Unexpectedly, I have discovered

5 .

10

15

25

30

35

that I can compensate for the loss of copper by adding from about 0.4 to 1.4 wt.% zinc and preferably about 0.5 to 0.8 wt.% Surprisingly, the added zinc provides sufficient strength to the new alloy while not producing any adverse corrosion resistance, toughness formability effects. By adding zinc in amounts below 0.4 wt.%, I do not obtain sufficient strength for highly specialized applications, such as fuselage skin, while adding zinc in amounts in excess of 1.4 wt.% tends to produce an alloy having undesirable density.

To produce the improved aluminum product, I first homogenize the alloy stock to produce a substantially uniform distribution of alloying elements. In general, I homogenize by heating the stock to a temperature raging from about 950 to 1050°F for a time period ranging from about 2 to 20 hours to dissolve soluble elements and to homogenize the internal structure of the metal. I caution, however, that temperatures above 1060°F are likely to damage the metal and thus I avoid these increased temperatures if possible. Generally, I homogenize for at least 10 hours in the homogenization temperature range. preferably, I homogenize for about 8 to 16 hours at a temperature of about 1030°F.

Next, I hot work the stock. Depending on the type of product I wish to produce, I either hot roll, extrude, forge or use some other similar hot working step. For example, I may extrude at a temperature ranging from about 800 to 950°F. My new alloy is well suited for making high quality sheet suitable for aircraft skin so my preferred

15

20

25

30

35

hot working step is to hot roll. To hot roll, I heat the stock to a temperature ranging from about 750 to 950°F for a time period ranging from about 2 to 10 hours. I generally perform hot rolling at a starting temperature ranging from about 750 to 900°F, or even higher as long as no melting or other ingot damage occurs. When the alloy is to be used for fuselage skins, for example, typically perform hot rolling on ingot starting stock 15 to 20 or more inches thick to provide an intermediate product having a thickness ranging from about 0.15 to 0.30 inches.

Depending on the type of sheet that I am producing, I may additionally cold roll after hot rolling to further reduce sheet thickness. Preferably, I allow the sheet to cool to less than 100°F and most preferably to room temperature before I begin cold rolling. Preferably, I cold roll to obtain at least a 40% reduction in sheet thickness, most preferably I cold roll to a thickness ranging from about 50 to 70% of the hot rolled gauge.

After cold rolling (or after hot rolling if I do not cold roll), I next solution heat treat the sheet. Preferably, I solution heat treat at a temperature ranging from about 1000 to 1080°F for a time period ranging from about 5 minutes to one hour. It is important to rapidly heat the stock, preferably at a heating rate of about 100 to 2000°F per minute. Most preferably, I solution heat treat at about 1020 to 1050°F for about 10 to 20 minutes using a heating rate of about 1000°F per minute.

If the solution heat treat temperature is substantially below 1020°F, then the soluble

15

20

25

30

elements, silicon, copper and magnesium are not taken into solid solution, which can have two undesirable consequences: (1) insufficient solute to provide adequate strength upon subsequent age hardening; and (2) copper and magnesium-containing intermetallic compounds that remain undissolved detract from fracture toughness, resistance, and corrosion resistance. Similarly, if the time at the solution heat treatment temperature is too short, these intermetallic compounds do not have time to dissolve. heating rate to the solutionizing temperature is important because relatively fast rates generate grain (crystallite) size, which desirable for good fracture toughness and high strength.

After solution heat treatment, I rapidly cool the stock to minimize uncontrolled precipitation of secondary phases, such as Mg₂Si. Preferably, I quench at a rate of about 1000 °F/sec. over the temperature range 750 to 550°F from the solution temperature to a temperature of 100°F or lower. Most preferably, I quench using a high pressure water spray at room temperature or by immersion into a water bath at room temperature, generally ranging from about 60 to 80°F.

At this point I can either obtain a T4 temper by allowing the product to naturally age or I can obtain a T6 temper by artificial aging. To artificial age, I prefer to reheat the product to a temperature ranging from about 300 to 400°F for a time period ranging from about 2 to 20 hours.

15

EXAMPLE 1

To demonstrate the present invention, I first prepared alloys of the compositions shown in Table 1 as DC (direct chill) cast ingots, which I then homogenized at 1025°F for 12 hours, cooled to room temperature, reheated to 900°F, hot rolled to 0.160 in. and cold rolled to 0.060 in. I then solution heat treated a portion of each sheet for 20 minutes at 1040°F, quenched in 70°F water and aged at 375°F for 6 hours (T6 temper).

TABLE 1. Chemical Compositions of Alloys Containing Manganese								
Alloy		 			,		% by	Wt.
No.	Si	Pe	Cu	Mn	Mg	Cr	Zn	Tr
1	0.76	0.17	0.28	0.43	0.94	<0.01	0.02	0.05
2	0.79	0.14	0.27	0.37	0.95	<0.01	1.15	0.02
3 . , .	0.77	0.14	0.51	0.37	0.93	<0.01	1,14	0.05
4 (6013)	0.75	0.17	0.88	0.42	0.95	<0.01	0.05	0.08

20 tested the artificially aged T6 temper materials tested for transverse tensile properties before and after a 30-day corrosive exposure to a NaCl solution (alternate immersion described in ASTM G-44). As recommended in the Corrosion Handbook (edited by H. H. Uhlig, John 25 Wiley & Sons, p. 956), I quantified corrosion damage by loss in ductility. This method is particularly suited to materials that susceptible to pitting and intergranular corrosion. I also tested the materials for Kahn 30

15

20

25

30

particularly suited to materials that are susceptible to pitting and intergranular corrosion. I also tested the materials for Kahn tear properties (unit propagation energy and tear strength_yield strength ratio), which are known to correlate with fracture toughness.

Next, I evaluated the naturally aged (T4 temper) sheets for formability under conditions of: (1) uniaxial stretching as measured by elongation in a standard tensile test, (2) biaxial stretching as measured by indenting the sheet with a 1-in. diameter steel ball (also known as Olsen cup depth), and (3) near-plane strain deformation as measured by stretching a narrow strip with a 2-in. diameter steel ball.

Table 2 shows the results of the tensile tests on the as-processed T6 temper materials.

TABLE	2. T	ransver Sheets	se Tensile Containing	Properties o Manganese	of T6 Temper
Alloy No.	% Cu	% Zn	Ultimate Tensile Strength,	Yield Strength, psi	Elongation % in 2-in.
			psi		
1	0.28	0.02	50.5	48.0	8.4
2]	0.27	1.15	52.6	50.3	7.8
3	0.51	1.14	56.5	53.2	9.0
4 (6013)	0.88	0.05	58.5	53.2	9.6

The data show that an alloy with about 0.50% copper and about 1.15% zinc has an equivalent yield strength to that of alloy 6013. It is also evident that the addition of about 1.15% zinc to

10

15

20

a base alloy containing about 0.25% copper increased its strength by about 2-2.5 ksi.

Table 3 gives the results of the tensile tests conducted on the corroded T6 temper sheets.

Alloy	% Cu	% Zn	% Elong	% Elongationb		ity Los
No.	l ° cu		Ave.	Min.	Ave.	Max.
1	0.28	0.02	8.1	8.0	3.6	4.1
2	0.27	1.15	6.7	6.2	14.1	20.
.3	0.51	1.14	7.7	6.5	14.4	27.1
4 (6013)	0.88	0.05	6.1	4.6	36.5	52.

The alloys containing about 0.25% to 0.5% copper and 1.15% zinc had much better corrosion resistance than 6013 alloy with 0.88% copper.

Table 4 gives the Kahn tear properties for the T6 temper sheets which I used to characterize the fracture toughness of the materials.

TABLE 4. Kahn Tear Properties of T6 Temper Sheets Containing Manganese								
Alloy No.	% Cu	% Za	Unit Prop'n Energy (in-lb/in²)	Tear Strength Yield Strength Ratio				
1	0.28	0.02	9.85	1.59				
2	0.27	1.15	821	1.49				
. 3	0.51	1.14	864	1.52				
4 (6013)	0.88	0.05	833	1.53				

25

30

15

20

25

These data show that the alloys with about 0.25% to 0.5% copper and 1.15% zinc have about equal toughness to alloy 6013.

Table 5 gives the results of the formability tests on the T4 temper materials.

•	TABLE 5. Formability of T4 Temper Sheets Containing Manganese								
Alloy No.	% Cu	% Zn	Longitudinal Elongation, %	Longitudinal Punch Depth, in.	Olsen Cup Depth, in.				
1	0.28	0.02	26.9	0.670	0.345				
2	0.27	1.15	27.1	0.690	0.340				
3	0.51	1.14	28.4	0.710	0.344				
4 (6013)	0.88	0.05	28.9	0.680	0.347				

The formability of the alloys with about 0.25% to 0.5% copper and 1.15% zinc were generally superior to the 0.28% copper base alloy and approximately equal to alloy 6013.

The foregoing results show that alloys with about 0.25% to 0.5% copper and 1.15% zinc have comparable strength, toughness and formability to alloy 6013, but have significantly improved corrosion resistance.

EXAMPLE 2

To demonstrate an alternative embodiment of my invention, I prepared alloys of the compositions shown in Table 6 in a similar manner to those in Example 1 except that they all contained about 0.15% chromium instead of manganese.

25

Alloy	٠			%	by Wt.		.5.	
No.	Si	Fe	Си	Mn	Mg	Cr	Zn	Ti
5	0.77	0.16	0.29	<0.01	0.93	0.15	0.73	0.05
6	0.74	0.14	0.27	<0.01	0.89	0.15	1.08	0.05
8	0.73	0.16	0.47	<0.01	0.91	0.14	1.03	0.03
7	0.75	0.17	0.44	<0.01	0.94	0.15	0.72	0.02

Next, I evaluated the alloys for formability (T4 temper), tensile properties, corrosion resistance and toughness by the same procedures that I used in Example 1. Table 7 gives the tensile properties for the T6 temper for these alloys.

TABLE 7. Transverse Tensile Properties of T6 Temper Sheets Containing Chromium								
Alloy No.	% Cu	% Zn	UTS (psi)	YS (psi)	% Elongation			
5	0.29	0.73	52.6	50.9	7.2			
6	0.27	1.08	52.1	50.1	7.5			
7	0.44	0.72	55.0	52.7	8.3			
8	0.47	1.03	55.3	52.7	8.3			

Allowing for the fact that alloys 6 and 8 had lower magnesium and silicon contents than the corresponding manganese-containing alloys 2 and 3 (Table 2), these materials had essentially equivalent strengths. It is apparent that a zinc concentration of about 0.7 wt.% is almost as effective as 1.1 wt.% level. This is important because the zinc concentration should be kept at its lowest possible level necessary to provide a strength advantage since higher concentrations increase the density of the alloy, which is undesirable for aerospace applications.

Table 8 gives the results of the tensile tests conducted on the corroded T6 temper sheets.

	. 10	remper 3	neets Co	ntaining Cl	iromium	
Alloy No.	% Çu	% Zn	% Elongation ^b		1	ectility oss
	·		Ave.	Min.	Ave.	Max.
5	0.29	0.73	6.9	6.4	4.2	, 11.1
6	0.27	1.08	7.1	6.8	5.3	9.3
7	0.44	0.72	7.2	7.0	13.3	15.7
8	0.47	1.03	8.1	7.6	2.4	8.4

Comparison of these results with those in Table 3 shows that the chromium-containing alloys have significantly superior corrosion resistance to the manganese-containing alloys.

Table 9 gives the Kahn tear (toughness) properties of the T6 temper sheets.

TABLE 9. Kahn Tear Properties of T6 Temper Sheets Containing Chromium							
Alloy No.	% Cu	% Zn	Unit Prop'n Energy (in-lb/in²)	Tear Strength- Yield Strength Ratio			
, 5	0.29	0.73	572	1.39			
6	0.27	1.08	613	1.44			
7	0.44	0.72	630	. 1.44			
8	0.47	1.03	675	1.42			

20

15

10

25

10

15

20

25

By comparison with Table 4, it is apparent that the chromiumcontaining alloys have lower fracture toughness than the manganesecontaining materials.

Table 10 lists the results of the formability tests on the T4 temper materials.

TABLE 10. Formability of T4 Temper Sheets Containing Chromium								
Alloy No.	% Cu	% Zn	Longitudinal Elongation (%)	Longitudinal Punch Depth (in.)	Olsen Cup Depth (in.)			
5	0.29	0.73	29.1	0.723	0.336			
6	0.27	1.08	29.1	0.722	0.321			
7	0.44	0.72	29.6	0.708	0.324			
8	0.47	1.03	29.6	0.704	0.327			

By comparison with Table 5, it is evident that the chromium-containing alloys have better longitudinal stretching capability than 6013 and the other manganese-containing alloys. Longitudinal punch depths (plane strain stretching) are about the same, whereas Olsen cup depths (biaxial stretching) are slightly lower.

Surprisingly, the Al-Mg-Si-Cu alloys in which I partially replaced the copper with zinc had much improved corrosion resistance while maintaining strength levels comparable to the 6013 type alloys. Figures 1 and 2 illustrate these results. Specifically, Figures 1 and 2 compare the corrosion resistance and strengths of such alloys with the relatively high copper alloy 6013. The invention alloys, which comprise manganese as the grain structure control agent, also have equivalent toughness and formability characteristics. The invention alloys, which contain chromium as the grain structure control agent,

have even further enhanced corrosion resistance with better uniaxial stretching capability in the T4 temper.

Having illustrated and described the principles of my invention in a preferred embodiment thereof, it should be readily apparent to those skilled in the art that the invention can be modified in arrangement and detail without departing from such principles. I claim all modifications coming within the spirit and scope of the accompanying claims.

10

25

CLAIMS

I claim:

- 1. A method of producing an aluminum product comprising:
- (a) providing stock including an aluminum base alloy consisting essentially of about 0.6 to 1.4 wt.% silicon, not more than about 0.5 wt.% iron, not more than about 0.6 wt.% copper, about 0.6 to 1.4 wt.% magnesium, about 0.4 to 1.4 wt.% zinc, at least one element selected from the group consisting of about 0.2 to 0.8 wt.% manganese and about .05 to 0.3 wt.% chromium, the remainder substantially aluminum, incidental elements and impurities;
 - (b) homogenizing the stock;
 - (c) hot working,
 - (d) solution heat treating; and
 - (e) quenching.
- 2. The method of claim 1 wherein the alloy of step (a) comprises about 0.7 to 1.0 wt.% silicon, not more than about 0.3 wt.% iron, not more than 0.5 wt.% copper, about 0.8 to 1.1 wt.% magnesium, and about 0.5 to 0.8 wt.% zinc.
- 3. The method of claim 2 wherein the alloy comprises about 0.3 to 0.4 wt.% manganese.
 - 4. The method of claim 2 wherein the alloy comprises about 0.1 to 0.2 wt.% chromium.
 - 5. The method of claim 1 wherein step (c) is selected from the group consisting of hot rolling at a temperature ranging from about 750 to 950°F, extruding at a temperature ranging from about 800 to 950°F, and forging.

20

- 6. The method of claim 1 further comprising natural aging to produce an improved alloy having good formability in a naturally aged T4 temper.
- 7. The method of claim 1 further comprising artificially aging to produce an improved alloy having good strength, toughness, and corrosion resistance properties.
 - 8. A product prepared by a process comprising the steps of:
- (a) providing stock including an aluminum base alloy consisting essentially of about 0.6 to 1.4 wt.% silicon, not more than about 0.5 wt.% iron, not more than about 0.6 wt.% copper, about 0.6 to 1.2 wt.% magnesium, about 0.4 to 1.4 wt.% zinc, at least one element selected from the group consisting of about 0.2 to 0.8 wt.% manganese and about .05 to 0.3 wt.% chromium, the remainder substantially aluminum, incidental elements and impurities;
 - (b) homogenizing the stock;
 - (c) hot working,
 - (d) solution heat treating; and
 - (e) quenching.
- 9. The product of claim 8 wherein the alloy of step (a) comprises about 0.7 to 1.0 wt.% silicon, not more than about 0.3 wt.% iron, about 0.3 to 0.5 wt.% copper, about 0.8 to 1.1 wt.% magnesium, and about 0.5 to 0.8 wt.% zinc.
 - 10. The product of claim 8 wherein the alloy comprises about 0.3 to 0.4 wt.% manganese.

15

20

25

()

- 11. The product of claim 8 wherein the alloy comprises about 0.1 to 0.2 wt.% chromium.
- 12. The method of claim 8 further comprising natural aging to produce an improved alloy having good formability in a naturally aged T4 temper.
- 13. The method of claim 8 further comprising artificially aging to produce an improved alloy having good strength, toughness, and corrosion resistance properties.
- 14. A method of producing an aluminum product having high formability, high fracture toughness, high strength and improved corrosion resistance, the method comprising:
- (a) providing stock including an aluminum base alloy consisting essentially of about 0.7 to 1.0 wt.% silicon, not more than about 0.3 wt.% iron, not more than about 0.5 wt.% copper, about 0.8 to 1.1 wt.% magnesium, about 0.3 to 0.4 wt.% manganese, and about 0.5 to 0.8 wt.% zinc, the remainder substantially aluminum, incidental elements and impurities;
- (b) homogenizing the stock at a temperature ranging from about 950 to 1050°F for a time period ranging from about 2 to 20 hours;
- (c) hot rolling at a temperature ranging from about 750 to 950°F will increase;
- (d) solution heat treating at a temperature ranging from about 1000 to 1080°F for a time period ranging from about 5 minutes to one hour;
- (e) cooling by quenching at a rate of about 1000°F/second to a temperature of 100°F or lower; and

- (f) artificially aging by reheating to a temperature ranging from about 300 to 400°F for a time period ranging from about 2 to 20 hours to produce a T6 temper in the aluminum product.
- 15. An aircraft fuselage skin produced by the method of claim 14.
 - 16. A product comprising an aluminum base alloy comprising about 0.6 to 1.4 wt.% silicon, not more than about 0.5 wt.% iron, not more than about 0.6 wt.% copper, about 0.6 to 1.2 wt.% magnesium, about 0.4 to 1.4 wt.% zinc, at least one element selected from the group consisting of about 0.2 to 0.8 wt.% manganese and about .05 to 0.3 wt.% chromium, the remainder substantially aluminum, incidental elements and impurities, the product having at least 5% improvement over 6013 alloy in corrosion resistance properties.
- 17. The product of claim 16 wherein the alloy comprises about 0.7 to 1.0 wt.% silicon, not more than about 0.3 wt.% iron, not more than 0.5 wt.% copper, about 0.8 to 1.1 wt.% magnesium, and about 0.5 to 0.8 wt.% zinc.
 - 18. The product of claim 16 wherein the alloy comprises about 0.3 to 0.4 wt.% manganese.
- 19. The product of claim 16 wherein the alloy comprises about 0.1 to 0.2 wt.% chromium
 - 20. The product of claim 16 having at least 25% improvement over 6013 alloy in corrosion resistance properties, as evidenced by loss of ductility after exposure to a salt-containing environment.

()

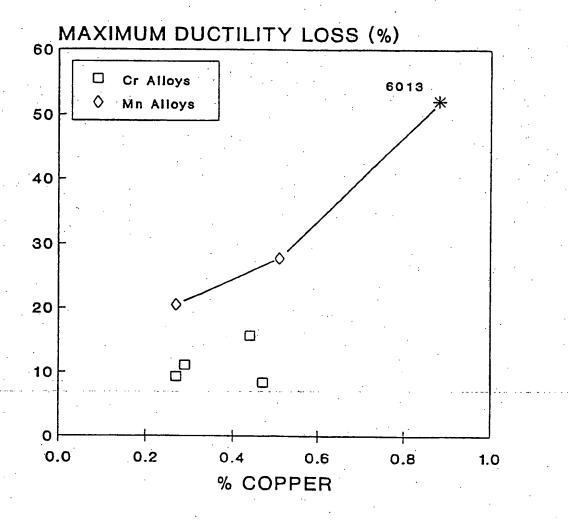


FIG. 1

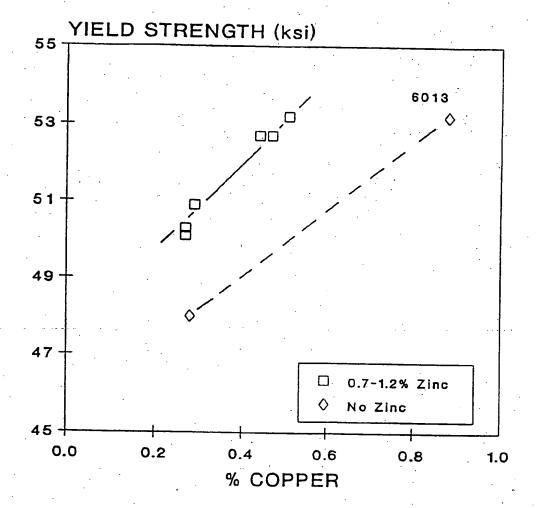


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No. PCT/US96/05327

IPC(6) US CL According to B. FIEL Minimum de	SSIFICATION OF SUBJECT MATTER :C22F 1/04 :Please See Extra Sheet. to International Patent Classification (IPC) or to both r .DS SEARCHED ocumentation searched (classification system followed)	by classification symbols)	
	148/689, 690, 692, 693, 694, 698, 701, 702, 417, 439 550, 553		
Documentat None	tion searched other than minimum documentation to the	extent that such documents are included	in the fields searched
Electronic d	lata base consulted during the international search (nar	ne of data base and, where practicable	search terms used)
None			
C. DOC	UMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where app	propriate, of the relevant passages	Relevant to claim No.
Y	JP, A, 6-240424 (SKY ALUM CO L English-language Abstract and col.		1-20
		·	
	·		
·			
Furti	her documents are listed in the continuation of Box C	. See patent family annex.	·
"A" do	secial categories of cited documents: comment defining the general state of the art which is not considered be of particular relevance rlier document published on or after the international filing date comment which may throw doubts on priority claim(s) or which is	"T later document published after the int date and not in conflict with the applic principle or theory underlying the "X" document of particular relevance; the considered novel or cannot be considered novel or cannot be considered to the document is taken alone.	ation but cited to understand the rention
sp O do	ted to establish the publication date of another citation or other ocial reason (as specified) ocument referring to an oral disclosure, use, exhibition or other cans	"Y" document of particular relevance; if considered to involve an inventive combined with one or more other auch being obvious to a person skilled in	s step when the document is the documents, such combination
-P- do	ocument published prior to the international filing date but later than a priority date claimed	'&' document member of the same pater	
Date of the	actual completion of the international search	Date of mailing of the international se	arch report
Commission Box PCT	mailing address of the ISA/US oner of Patents and Trademarks on. D.C. 20231	DAVID A. SIMMONS CO	Thomas

INTERNATIONAL SEARCH REPORT

International application No. PCT/US96/05327

A. CLASSIFICATION OF SUBJECT MATTER: US $\operatorname{CL}\,:$

148/689, 690, 692, 693, 694, 698, 701, 702, 417, 439, 440; 420/532, 534, 537, 538, 541, 544, 545, 546, 547, 548, 550, 553

Form PCT/ISA/210 (extra sheet)(July 1992)*

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

BLACK BORDERS

IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

FADED TEXT OR DRAWING

BLURRED OR ILLEGIBLE TEXT OR DRAWING

☐ SKEWED/SLANTED IMAGES	
☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS	
☐ GRAY SCALE DOCUMENTS	
☐ LINES OR MARKS ON ORIGINAL DOCUMENT	
☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE PO	OR QUALITY
☐ OTHER:	

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.